

Relaxation Dynamics of H₂O and H₂S Following Excitation of 1s Core Electrons

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INTRODUCTION

Mass spectroscopy of atoms and molecules is a relatively well-understood technique [1-2]. Coupled with high brightness and high resolution synchrotron-radiation (SR) sources, this technique has proven useful in elucidating some of the multitude of electronic and fragmentation decay pathways available to core-excited systems. To date, the vast majority of these studies have concentrated on relaxation of systems following excitation of a shallow-core electron, where shallow-core levels are those which can decay electronically only through interaction with valence-shell electrons (e.g., S 2*p*, O 1*s*). In contrast, deep-core holes (e.g., Cl 1*s*, S 1*s*) have shorter lifetimes and typically

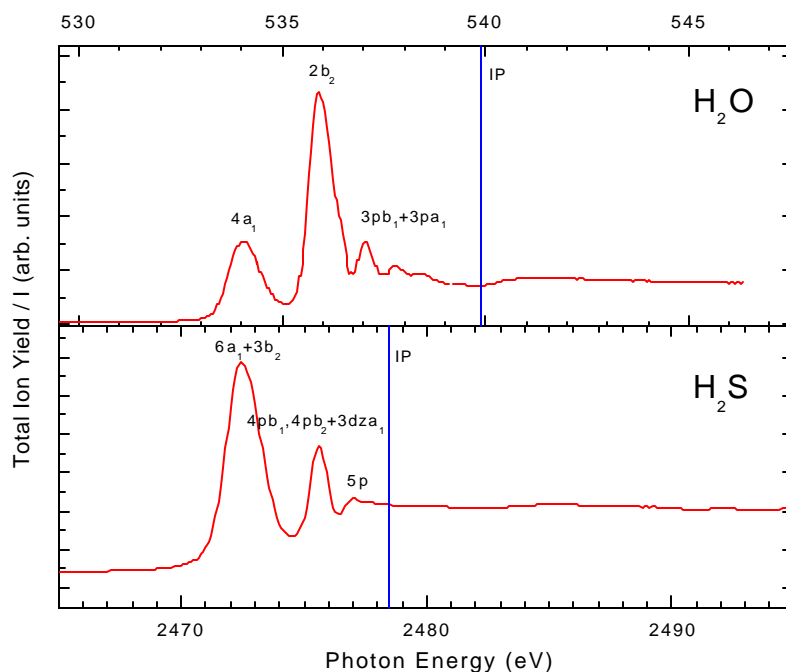


Fig. 1 Total ion yield spectra for H₂O and H₂S.

relax through Auger decay to create shallow-core holes. Because of this extra decay step, deep-core-excited systems have a much wider array of pathways by which they can relax and usually produce much more highly charged residual ions by means of a stepwise series of decays known as a vacancy cascade [3].

Gas-phase H₂O and H₂S serve as interesting systems to study for a number of reasons. In both cases, the core-level spectroscopy is well understood [4-6] and electron-spectroscopy measurements [7-8] have been performed. As non-metals in the same column of the periodic table, oxygen and sulfur have the same valence structure with different noble gas cores (Ne and Ar respectively). In addition, the molecules have the same symmetry but different bond angles (H₂O 104.5°; H₂S 92°). Thus comparisons of the spectroscopy of the two molecules help to elucidate electron correlation effects in order to determine the changes in resulting fragmentation kinematics.

EXPERIMENT

The H₂S measurements were performed using x-ray synchrotron radiation from BL 9.3.1 at the Advanced Light Source (ALS)[9-11], a bending magnet beamline covering the range 2-5 keV with a resolution ($E/\Delta E$) \approx 7500. Water measurements were performed at BL 6.3.2, another bending magnet beamline covering the 100-1200eV range with a resolution ($E/\Delta E$) \approx 8000. In both instances an absorption or gas cell was utilized. An extraction voltage (approximately 200V) was applied to a plate pushing the ions from the interaction region onto a collector plate. The resulting current was monitored with a Keithley picoammeter while changing the photon energy.

RESULTS

The ground-state electronic configuration of H₂O is

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2.$$

The oxygen $2p_z$ and $2p_y$ combine with the H $1s$ orbitals to form the $3a_1$ and $1b_2$ orbitals which comprise the O-H bonds. For comparison, the ground-state electronic configuration of H₂S is

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 \quad 4a_1^2 2b_2^2 5a_1^2 2b_1^2.$$

Fig. 1 shows the total-ion yield spectra for both H₂O and H₂S. In H₂O the three largest peaks at 534.0, 535.9, and 537.1 eV result from excitations of O $1s$ electrons to the $4a_1$, $2b_2$, and $3pb_1+3pa_1$ resonances, respectively. In H₂S the lowest energy and most intense peak is derived from S $1s$ excitations to the $6a_1$ and $3b_2$ orbitals, with the a_1 orbital being only about 20% as intense as the b_2 . The second peak is derived from S $1s$ excitations to the $4pb_1$, $4pb_2$ and $3d_{z^2}$ orbitals. The third and least intense peak is derived from S $1s$ excitations to $5p$ derived Rydberg orbitals. Examination of the spectra in Fig. 1 shows a striking difference between the relative intensities of the different resonances. This is in spite of the fact that in both cases the electrons are being excited to molecular orbitals of the same character.

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